

BEST AVAILABLE COPY

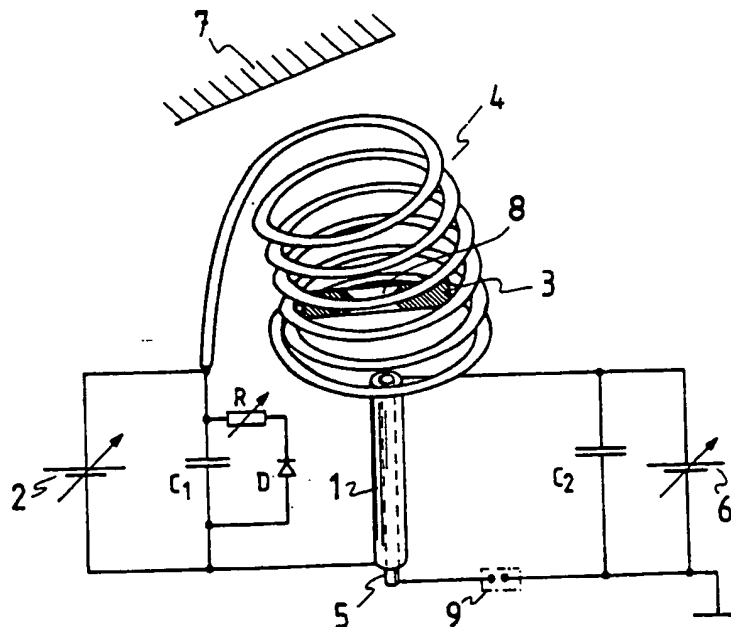
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>4</sup> :</b> <b>C23C 14/22, 14/32, H01J 37/32</b> <b>H05H 1/50</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 89/ 06708</b> <b>(43) International Publication Date:</b> 27 July 1989 (27.07.89)
<b>(21) International Application Number:</b> PCT/FI89/00008 <b>(22) International Filing Date:</b> 18 January 1989 (18.01.89) <b>(31) Priority Application Number:</b> 880203 <b>(32) Priority Date:</b> 18 January 1988 (18.01.88) <b>(33) Priority Country:</b> FI  <b>(71)(72) Applicants and Inventors:</b> ANTILA, Asko [FI/FI]; Mustikkasuontie 17, SF-00940 Helsinki (FI). HIR- VONEN, Juha-Pekka [FI/FI]; Vanamonkuja 1 A 6, SF-01350 Vantaa (FI). KOSKINEN, Jari [FI/US]; 546 Warren rd Apt 2, Ithaca, NY 14850 (US).  <b>(74) Agent:</b> PATENTTITOIMISTO OY HEINÄNEN AB; Annankatu 31-33 C, SF-00100 Helsinki (FI).		<b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (Eu- ropean patent), CM (OAPI patent), DE, DE (Euro- pean patent), DK, FR (European patent), GA (OAPI patent), GB, GB (European patent), HU, IT (Euro- pean patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI pa- tent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>

**(54) Title:** PROCEDURE AND APPARATUS FOR THE COATING OF MATERIALS BY MEANS OF A PULSAT-  
ING PLASMA BEAM

**(57) Abstract**

Procedure and apparatus for the coating of materials, in which procedure the material (7) is coated by means of a pulsating plasma beam emitted from at least one electrode (1), said plasma beam being accelerated by a magnetic field and deflected by same to separate the uncharged particles from it, whereupon the plasma beam hits the surface of the material (7) to be coated. The apparatus of the invention for the coating of materials is provided with electrodes (1, 3), at least one voltage source (2) and at least one capacitor (C1) for producing a pulsating plasma beam and at least one deflected coil (4) which generates a magnetic field that accelerates said plasma beam emitted by at least one electrode (1) and deflects the beam to separate the uncharged particles from it.

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

WO 89/06708

1

PCT/FI89/00008

Procedure and apparatus for the coating of materials  
by means of a pulsating plasma beam

The present invention relates to a procedure and an apparatus for the coating of materials.

Coatings consisting of or resembling a diamond material have properties similar to corresponding traditional diamonds. The first property is hardness. Another significant mechanical property is a low friction coefficient. The resistance to wear is also extraordinary. Furthermore, such a coating remains unchanged in all known kinds of acid and base. Diamond and diamond-like materials are therefore especially suited for the coating of objects subject to wear or corrosion, e.g. bearings without lubrication. A further notable factor is the high refraction index of diamonds.

In microelectronics, the high thermal capacity and thermal conductivity of diamond and diamond-like coatings provide significant advantages. To achieve higher component densities and speeds, it is necessary to reduce the structural size of integrated circuits. This makes it more difficult to remove the heat generated by the electric current, and it also means that good conductivity is more important than before.

In current practice, diamond-like coatings are produced by direct ion beam treatment, which is based on increasing the energy of ions. In direct ion beam coating, the coat is grown on the surface of the object material directly from the ion beam, from which the impurities have been removed by means of a separating magnet. The worst problem with this method is the difficulty of constructing an ion source of sufficient capacity. Another currently used method for growing a diamond coat is based on plasma-assisted vapour phase coat deposition (PAVCD). In this method, a crystalline diamond is grown from a mixture of methane and hydrogen. Unlike the method based on the use of an energetic ion

WO 89/06708

2

PCT/FI89/00008

beam for growing a diamond coat, which can be implemented in room temperature, the PAVCD method requires a high temperature of the order of 800°C. This is a serious disadvantage in view of the coating of conventional materials used in tools or construction.

The object of the present invention is to eliminate the drawbacks referred to above. The procedure of the invention for the coating of materials is characterized in that the material is coated using a pulsating plasma beam obtained from at least one electrode, said plasma beam being accelerated by a magnetic field and deflected by same to separate the uncharged particles from it, whereupon the plasma beam hits the surface of the material to be coated.

The advantages of the procedure are that it is simple and enables even large surfaces to be coated.

A preferred embodiment of the procedure of the invention is characterized in that the plasma beam consists of particles emitted from at least one electrode.

Another preferred embodiment of the procedure of the invention is characterized in that the coating is performed in a vacuum.

Another preferred embodiment of the procedure of the invention is characterized in that the coating process uses a gaseous medium which reacts with charged particles.

Another preferred embodiment of the procedure of the invention is characterized in that the plasma beam is deflected by a magnetic field produced by means of a deflected coil.

The apparatus designed for implementing the procedure of the invention for the coating of materials is characterized in that, for the coating of a material, the apparatus is

WO 89/06708

3

PCT/FI89/00008

provided with electrodes, at least one voltage source and at least one capacitor for producing a pulsating plasma beam and at least one deflected coil which generates a magnetic field that accelerates said plasma beam emitted by at least one electrode and deflects the beam to separate uncharged particles from it.

A preferred embodiment of the apparatus designed for implementing the procedure of the invention is characterized in that, to prevent oscillation of the voltage, the apparatus is provided with a diode connected in parallel with the capacitor.

Another preferred embodiment of the apparatus designed for implementing the procedure of the invention is characterized in that it is provided with at least one igniter circuit to produce an arc between the electrodes.

Another preferred embodiment of the apparatus designed for implementing the procedure of the invention is characterized in that at least one of the electrodes is of a cylindrical form.

Another preferred embodiment of the apparatus designed for implementing the procedure of the invention is characterized in that at least one of the electrodes is placed wholly or partially inside the coil.

Another preferred embodiment of the apparatus designed for implementing the procedure of the invention is characterized in that at least one of the electrodes is provided with at least one hole through which the plasma beam is directed.

Another preferred embodiment of the apparatus designed for implementing the procedure of the invention is characterized in that the igniter circuit comprises a metal rod

WO 89/06708

4

PCT/FI89/00008

inside each cylindrical electrode, another capacitor and a voltage source, which are used to produce an igniting arc between said electrode and said rod.

Another preferred embodiment of the apparatus designed for implementing the procedure of the invention is characterized in that the igniter circuit has at least one external spark gap or switch.

In the following, the invention is described by the aid of an example with reference to the attached drawing, which represents a plasma accelerator and an object to be coated. For the coating of a material, the plasma accelerator produces a cloud of plasma from carbon. This cloud is accelerated towards the object to be coated, and deflected by the magnetic field, whereupon the plasma beam strikes the surface of the object. Both the plasma accelerator and the object to be coated are placed in a vacuum. The plasma accelerator has a cylindrical cathode 1 made of solid carbon, which is connected to the negative terminal of the first voltage source 2 and to the first terminal of the first capacitor C1. The disc-shaped anode 3, which has a hole in the middle, is connected to a cylindrical coil 4 formed from a copper conductor. The coil is deflected and connected at one end to the positive terminal of the first voltage source 2 and to the other terminal of the first capacitor C1. Connected to the terminals of the capacitor C1 are also a diode D and a variable resistor R. The cathode 1 is partially and the anode 3 wholly inside the coil 4.

Inside the cathode 1 is a metal rod 5. The cathode 1 and the rod 5 together form a second voltage source 6 and, together with a second capacitor C2, an igniter circuit. The second voltage source 6 is variable. The cathode 1 is connected to the positive terminal of the second voltage source 6 and to the first terminal of the second capacitor C2. The metal rod 5 is connected to the negative terminal

WO 89/06708

5

PCT/FI89/00008

of the second voltage source 6 and to the other terminal of the second capacitor C2.

The plasma accelerator performs the coating of a metal plate 7 as follows. The first voltage source 2 charges the first capacitor C1, connected in parallel with the voltage source. The second voltage source 6 charges the second capacitor C2, likewise connected in parallel with it, until a spark-over occurs across the air gap between the cathode 1 and the metal rod 5, so that an arc is generated in said air gap. This arc discharges the second capacitor C2 and correspondingly produces an arc between the cathode 1 and the anode 3. As a result, the cathode begins to emit a beam of carbon particles consisting of charged ions and uncharged atoms. The arc between the cathode 1 and the anode 3 discharges the first capacitor C1, and the arc is extinguished when the capacitor voltage falls below the level required for maintaining the arc. In this manner, a pulsating plasma beam is produced from carbon ions and carbon atoms. The duration of a pulse is determined by the capacitance of the first capacitor C1.

Connected in parallel with the first capacitor C1 are a diode D, whose function is to remove the reverse voltage produced across the first capacitor C1 by the oscillating circuit consisting of capacitor C1 and coil 4, and a variable resistor R protecting the diode D.

The plasma beam is accelerated through the magnetic field generated by the winding 4. Since the coil 4 has a curved shape, the charged ions passing through the hole 8 in the anode 3 will follow the curvature of the magnetic field, whereas uncharged particles will proceed straight past the plate 7. In this manner, uncharged particles are separated from the charged ions. The plate 7 to be coated is placed close to that end of the coil 4 which is connected to the first voltage source 2 and the first capacitor C1. Since

WO 89/06708

6

PCT/F189/00008

the magnetic field generated by the coil 4 diverts the charged ions but does not affect the passage of uncharged particles, the plate to be coated is only struck by ions accelerated by the magnetic field.

When an ion with sufficient energy, imparted by the magnetic field, hits the surface of the plate 7, it is able to penetrate into the surface material. In the course of the next 10-11 s., the microscopic area around the penetrating ion undergoes remarkable changes. A significant proportion of the atoms in the plate surface have been displaced from their normal lattice positions, and the proportion of vacancies and interstitial atoms may reach a level of several per cent. The conditions inside a cascade like this correspond to a temperature of several thousand °C, although the ambient temperature remains unchanged. Moreover, the pressure at the edges of the cascade increases. As a result of the process described, a diamond-like coat is produced on the surface of the plate 7.

Instead of a vacuum, it is also possible to use a gaseous medium which reacts with the ions in the surface of the material to be coated, producing e.g. a coat of boron nitride. In the igniter circuit, the arc between the cathode 1 and the metal rod 5 is automatically extinguished when the voltage across the second capacitor C2 falls below the level required for maintaining the arc. The igniter circuit may also employ an external spark gap 9 or switch to extinguish the arc between the cathode 1 and the metal rod 5 at a desired moment.

It is obvious to a person skilled in the art that different embodiments of the invention are not restricted to the examples described above, but that they may instead be varied within the scope of the following claims.



WO 89/06708

7

PCT/FI89/00008

## CLAIMS

1. Procedure for the coating of materials, characterized in that the material (7) is coated by means of a pulsating plasma beam proceeding from at least one electrode (1), said plasma beam being accelerated by a magnetic field and deflected by same to separate the uncharged particles from it, whereupon the plasma beam hits the surface of the material (7) to be coated.

2. Procedure according to claim 1, characterized in that the plasma beam consists of particles emitted from at least one electrode (1).

3. Procedure according to claim 1 or 2, characterized in that the coating process takes place in a vacuum.

4. Procedure according to claim 1 or 2, characterized in that the coating process uses a gaseous medium which reacts with the charged particles.

5. Procedure according to any one of the claims 1 - 4, characterized in that the plasma beam is deflected by a magnetic field generated by means of a deflected coil (4).

6. Apparatus designed for implementing the procedure of claim 1 for the coating of materials, characterized in that, for the coating of a material, the apparatus is provided with electrodes (1,3), at least one voltage source (2) and at least one capacitor (C1) for producing a pulsating plasma beam and at least one deflected coil (4) which generates a magnetic field that accelerates said plasma beam emitted by at least one electrode (1) and deflects the beam to separate uncharged particles from it.

WO 89/06708

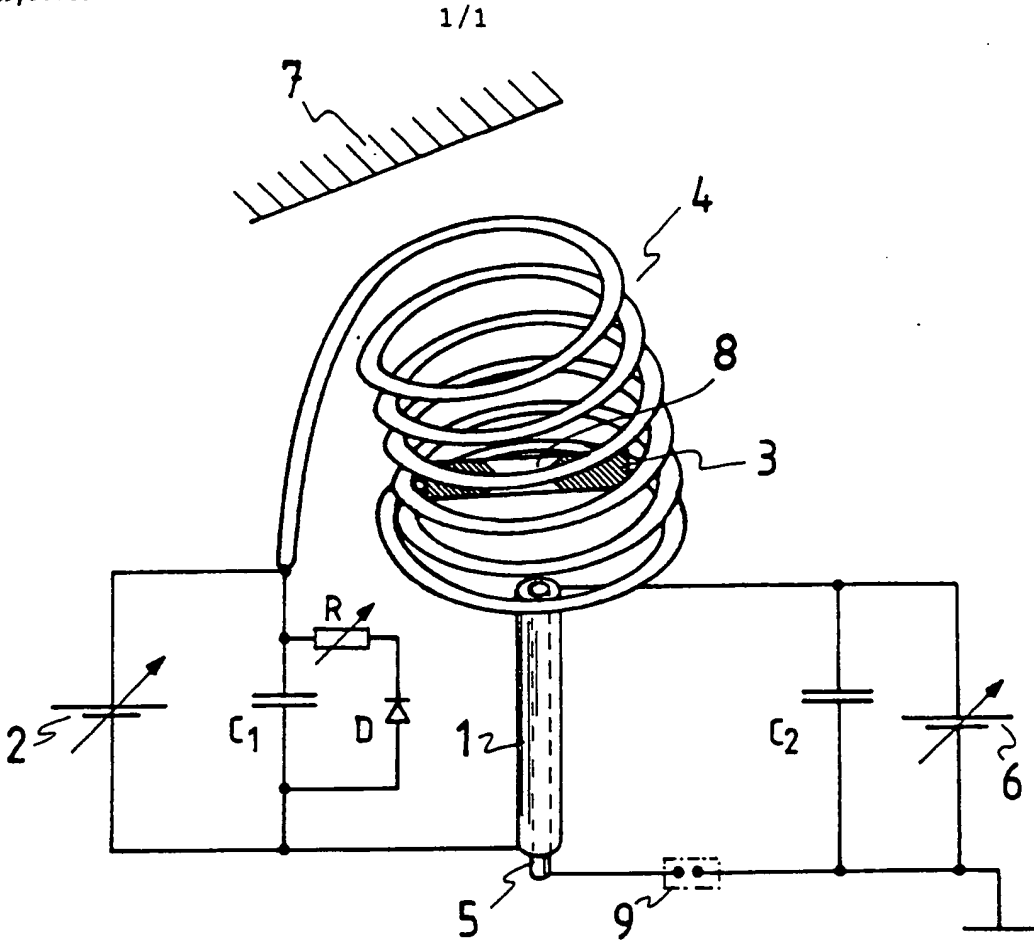
8

PCT/FI89/00008

7. Apparatus according to claim 6, characterized in that, to prevent oscillation of the voltage, a diode (D) is connected in parallel with the capacitor (C1).
8. Apparatus according to 6 or 7, characterized in that it is provided with at least one igniter circuit to produce an arc between the electrodes (1,3).
9. Apparatus according to claim 6, 7 or 8, characterized in that at least one of the electrodes (1) is of a cylindrical form.
10. Apparatus according to claim 6, 7, 8 or 9, characterized in that at least one of the electrodes (1,3) is placed wholly or partially inside the coil (4).
11. Apparatus according to any one of the claims 6 - 10, characterized in that at least one (3) of the electrodes is provided with at least one hole (8) through which the plasma beam is directed.
12. Apparatus according to any one of the claims 6 - 11, characterized in that the igniter circuit comprises a metal rod (5) inside each cylindrical electrode (1), another capacitor (C2) and a voltage source (6), which are used to produce an igniting arc between said electrode (1) and said rod (5).
13. Apparatus according to any one of the claims 6 - 12, characterized in that the igniter circuit is provided with at least one external spark gap (9) or switch.

WO 89/06708

PCT/F189/00008



## INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 89/00008

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC <sup>4</sup>		
C 23 C 14/22, /32, H 01 J 37/32, H 05 H 1/50		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC 4	C 23 C 14/00, /22, /32, /34, /48; H 01 J 37/317, /32, /34; H 05 H 1/50	
US Cl.	118: 50.1; 204: 192, 298; 427: 37	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>		
SE, NO, DK, FI classes as above		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	SE, B, 430 293 (I I A KHARKOV et al.) 31 October 1983 see abstract, fig 1, page 2, lines 1-25	1,2,3,5,6,8, 9,11
Y	SE, B, 450 539 (GENNADY VASILIEVICH KLJUCHKO et al.) 29 June 1987 see abstract, fig 1 and 4, claims 1, 3, 4, 7 page 1, line 8 - page 2, line 26	1,2,3,8,9,10, 11
Y	EP, A1, 0 225 680 (ANDAL CORP.) 16 June 1987 see abstract, fig 1 & US, 4620913 JP, 62120472	2,3,4,8,9,11
Y	US, A, 4 645 895 (BOXMAN et al.) 24 February 1987 see column 1, lines 10-18, lines 40-48, column 7, lines 14-60, column 11, lines 31-37, column 14, lines 13-68 & DE, 3513014 JP, 61099672 .../...	1,2,3,4,6,8,9, 10,12
<p><sup>9</sup> Special categories of cited documents: 18</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
1989-04-11	1989-04-13	
International Searching Authority	Signature of Authorized Officer	
Swedish Patent Office	Ingrid Grundfelt	

International Application No. PCT/FI 89/00008

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	Proceedings of the IEEE, Vol. 60, No 8, August 1972, page 977-991, "PULSED METALLIC-PLASMA GENERATORS", Alexander S Gilmour Jr and David L Lockwood, see abstract, fig 5, 6, 8(b) and 15(b), page 983	1,2,3,5,6,8, 9,10,11,12
A	US, A, 4 490 229 (MIRTICH et al.) 25 December 1984	
A	US, A, 4 565 618 (BANKS) 21 January 1986	

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER: \_\_\_\_\_**

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**